with lithium aluminium deuteride in dry oxolane (tetrahydrofuran) at 70°C for 16 h. The ester residue is then converted to a 6,6-dideuteriohexose residue, the O-methyl ethers of which are easily distinguishable by GC-MS of the derived alditol acetates.

An alternative to acid hydrolysis that is applicable to most polysaccharides and glycoconjugates, including those containing acid-labile residues or glycosidic linkages resistant to hydrolysis, is afforded by methanolysis, in which the sample is heated in methanolic HCl, the conditions employed depending upon the nature of the sugar residues present. After suitable derivatization, all components of methanolysates, now present as methyl glycosides or, in the case of hexuronic acids, methyl glycoside methyl esters, can be analysed simultaneously, either by GC (Table 2) or by LC (Table 3). The procedure is also applicable to methylation analysis, the methylated methyl glycosides and methyl glycoside methyl esters being amenable to GC without further derivatization (Table 2).

See Colour Plate 118.

See also: **II/Chromatography:** Paper Chromatography. **Chromatography: Gas:** Derivatization; Detectors: Mass Spectrometry. **Chromatography: Liquid:** Derivatization. **Chromatography: Thin-Layer (Planar):** Spray Reagents. **III/Impregnation Techniques: Thin-Layer (Planar) Chromatography. Polysaccharides:** Centrifugation; Liquid Chromatography.

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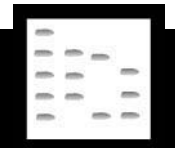
SULFUR COMPOUNDS: GAS CHROMATOGRAPHY



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Introduction

Sulfur compounds, of both biogenic and anthropogenic origin, constitute a large group of compounds, ranging from simple gases up to complex polycyclic aromatics. These compounds can be present in various, usually complex matrices, such as air (gaseous), water systems (aqueous), various petroleum fractions (gaseous, liquid and solid), in beverages and foodstuffs and in pharmaceutical formulations.

Environmentalists believe that these compounds are responsible for the damage of our environment through acid deposition, rapid acidification of lakes, the loss of forests, the corrosion of metal structures and historical monuments. The interest in biogeochemistry results from the role some sulfur compounds play in global chemical cycles. Dimethyl sulfide (DMS) in sea water, produced in the oceans, is believed to play a critical role in the global sulfur cycle and the radiation balance of the Earth. Also, other sulfur compounds may contribute significantly to the sulfur flux in the atmosphere. In foods, beverages and in water, trace levels of sulfur-containing compounds are responsible for taste and odour problems. They are also the source of malodorous conditions in municipal sewage systems. Refiners worldwide give particular attention to these compounds because in petrochemical and chemical applications even trace levels of sulfur impurities may cause concern. They can poison the catalysts, impart

undesirable properties to final products or produce general air pollution when fuel is burnt.

For these reasons sulfur-containing compounds are of constant concern in many fields. Gas chromatography, due to combination of separation capability and sensitive detection is still a prime technique for the analysis of these compounds in various matrices.

General Problems of the Determination of Sulfur Compounds by Gas Chromatography

The analysis of sulfur compounds in different environmental matrices is still a big challenge for the analytical chemist. The main difficulties in their determinations are related to the two main obstacles.

The first is common with general problems encountered in trace analysis. Most of these compounds are present at low concentrations, frequently at the low parts per trillion (ppt) level. They may be encountered in very complex matrices and in a broad range of concentrations (often several orders of magnitude). Complex mixtures can cause interference problems between major and minor constituents.

The second difficulty is due to the highly reactive nature of sulfur compounds. It is well known that these compounds have absorptive, adsorptive, photooxidative and metal catalytic oxidative features. This can lead to irreversible adsorption, reaction with each other, catalytic reactions, rearrangements catalysed by different materials and reactions with substances they come into contact with. Because of these reasons special precautions should be undertaken during all steps of their analysis, e.g., during sample treatment (sampling, storage, pre-concentration and isolation) as well as during the gas chromatographic analysis.

When sulfur content is relatively high (up to percentage level) and the matrix is very complex, like crude oil, direct GC analysis can be frequently done, reducing the analysis time and eliminating the possibility of analyte losses. Such samples, due to possible interference problems, require very effective separation systems and very selective (specific) detectors. The choice of a detector with high selectivity for sulfur over hydrocarbon is crucial.

Due to the diversity of the matrices in which sulfur compounds can be present it is convenient to discuss each type of sample separately.

Atmospheric Sulfur Gases

Sulfur gases are released into the atmosphere from various natural and anthropogenic sources. The most abundant atmospheric sulfur compounds are: hydrogen sulfide (H_2S), carbonyl sulfide (COS), dimethyl sulfide (DMS), dimethyldisulfide (DMDS), carbon disulfide (CS_2) and methanethiol (methyl mercaptan – MeSH). These compounds have received a great deal of attention because of the suggestion that the emission of natural compounds may be substantial even compared to anthropogenic sources of sulfur dioxide (SO_2). Frequently, all these compounds are called 'reduced sulfur compounds', S(-II), abbreviated to RSCs. These compounds, together with other sulfur species with boiling points up to ca. 200°C, are usually termed 'volatile sulfur compounds' (VSCs). Considering VSCs the emphasis is especially put on DMS, which is the predominant form of volatile sulfur compounds in the oceans.

Sampling

Sampling vessels (glass bottles, bulbs, canisters and polymeric bags) for sulfur gases should be as inert as possible in order to minimize adsorption losses and to avoid possible reactions during sampling. For these reasons, all materials in sampling vessels, tubing and unions in contact with the sample should be carefully chosen. The conditioning or covering of surfaces with inert materials or application of surface deactivation procedures such as silanization is usually necessary.

Glass sampling bottles or bulbs are commonly used for collecting and transporting gas samples or to blend calibration gas mixtures. Stainless steel canisters and Teflon bottles are very convenient. Frequently, the canisters are conditioned by heating under vacuum before use. Sampling bags made of Tedlar film which is a polyvinyl fluoride (PVF) are chosen because of their inertness. To prevent losses of sulfur compounds, sampling vessels and connections may be covered with aluminium foil to avoid photochemical reactions.

Preconcentration

Due to the low concentration of sulfur species in air (ppb or ppt level) different preconcentration techniques have been applied before the gas chromatographic analysis proper. The most frequently used methods for these purposes are sorption on certain metals, sorption on solid sorbents and cryogenic trapping.

Sorption on metals This pre-concentration method is based on the ability of certain metals (mainly gold, palladium and platinum) to chemisorb sulfur gases. Glass or quartz tubes filled with gold wool, gold-coated glass beads, gold-plated sand or metal foils are used for this purpose. The sample may be passed through a Teflon tube containing a thin metal foil of

palladium (Pd), platinum (Pt) or gold (Au). Custom-fabricated Pd on Pt has the advantage of the analytical collection efficiency of Pd and an increased durability and lifetime. Rapid desorption of the sulfur compounds is achieved by passing a current through the foil. Such a technique (metal foil collection/flash desorption and flame photometric detection) has demonstrated a detection limit for total sulfur concentration of around 10 pptv (10^{-11}).

Sorption on solid sorbents Adsorption on solid sorbents is one of the simplest and most efficient methods of concentration of volatile compounds. Adsorbent trapping is very popular, especially when traps are kept at low temperatures. Ambient temperature trapping may frequently give poor recoveries due to poor collection efficiency.

Many sorbents, such as activated charcoal, silica gel, aluminium oxide, graphitized carbon black, molecular sieves and porous polymers have been applied to collect volatile sulfur species. The use of porous polymers is the most widespread since the collected substances can be desorbed from porous polymers more easily, compared to desorption from charcoal. Furthermore, collection efficiency on porous polymers is less sensitive to water vapour in the sampling atmosphere. The trapped compounds are usually released by thermal desorption and injected into a GC column. Before this operation, they may be subjected to cryothermal focussing in a capillary in order to obtain a narrow injection band.

Among the porous sorbents, Tenax has the highest popularity. Tenax has a low affinity for water, and breakthrough volume is relatively independent of humidity. It is well suited for thermal desorption techniques as it exhibits high thermal stability (375°C) and can be subjected to repeated temperature cycling without deterioration. The determination of several sulfur gases can be easily conducted, even though Tenax has a relatively low specific surface area (ca. 19 m^2/g) which consequently limits the sampling volume. In practice, Tenax GC or TA is used together with Chromosorb 106 and Spherocarb as backup adsorbents. In order to retain the low boiling organic sulfur compounds that are present in many samples, cooling the trap with liquid nitrogen may be necessary but this creates a problem when excessive amounts of methane are present. Cooling with solid carbon dioxide is suitable for trapping of VOS compounds under these circumstances. Carbosieve adsorption tubes can be used for collecting CS_2 after purging it from seawater samples.

For moist air samples (96% relative humidity) acceptable recoveries have been observed for the following sorbents: silica gel (recovery for MeSH $> 95\%$), molecular sieve (recovery for MeSH 73.9% for COS 75%) and Carbosieve III S (recovery for COS 71.7%) used with calcium chloride as a drying agent. For methanethiol, recovery values showed no significant changes during 36 h storage or using different flow rates in the range of 10–80 mL min^{-1}.

Cryogenic trapping Cryogenic trapping is the technique of choice for collecting VSCs from air samples but is not always practical due to transportation and storage difficulties at remote locations.

Cryogenic trapping is very popular after purging VSCs from various water samples and therefore is also discussed in the next section.

Analysis of VSCs in air is complicated by the oxygen, SO_2 and NO_2 which can cause variable and often severe sampling losses by oxidation of these compounds. Scrubbers for oxidant removal include Teflon and Tygon shavings, and various substrates (glass fibre filters, Chromosorb, Anakrom, and glass beads) coated with Na_2CO_3 or manganous oxide, MnO.

Sulfur Compounds in Aqueous Matrices

Sampling

Aqueous samples for the analysis of VSCs are usually collected in glass or polymer bottles. Glass vessels are frequently silanized in order to minimize losses due to adsorption on the walls. Brown glass is used to stop biological and chemical processes which can occur under the influence of light. Teflon and polyethylene are frequently used. During sampling the vessels should be filled to the top to exclude air and minimize head space losses.

Isolation and/or Preconcentration

Because direct analysis of sulfur compounds in water matrices is often impossible, various preconcentration or isolation procedures are applied before the analysis proper. Solvent extraction and static and dynamic headspace techniques are most popular.

Liquid extraction Solvent extraction is not as frequently applied as formerly because this technique has several disadvantages, i.e., handling toxic solvents, the trapped substances become diluted, automation is difficult and the procedures are time consuming. The most popular solvents for the VSCs are diethyl ether, hexane or mixtures of these solvents.

Static gas extraction methods Headspace-gas chromatography (HS-GC) analysis can be applied

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successfully for the analysis of VSCs in different liquid matrices. It can be also applied in physical chemistry studies of these compounds, being a valuable tool for acquiring data on gas–solid and gas–liquid systems. For example, it was used for the determination of distribution coefficients, K, of selected organosulfur compounds in air–water systems as well as their temperature, ionic strength and concentration dependencies.

Generally, the detection limit of the static headspace technique is 10 to 100 times poorer than that of the dynamic technique, i.e., purge and trap (PT).

Dynamic gas extraction methods Purge and trap assemblies can be used for isolation and preconcentration of volatile sulfur species in water samples. The extraction efficiency varies with the gas considered and the extraction facilities employed such as the dimensions of the purge vessel, bubble size distribution, sample volume and temperature, purge gas flow rate and sparge time. All these parameters should be carefully considered before applying the technique for a particular purpose.

Due to the low detection limits which can be obtained with the PT technique, it is extensively used to determine VSCs in water. Several PT procedures have been developed especially for the most important natural sulfur compound – dimethyl sulfide (DMS) – a climatically active trace gas.

Recently, there has been an interest in dimethyl sulfoxide (DMSO) determination. DMSO is also an environmentally significant compound because of its potential role in the biogeochemical cycle of DMS. Direct injection and separation of aqueous DMSO offers a simple and fast application, but exhibits limited sensitivity due to limitation on injection volumes. More frequently, DMSO reduction and subsequent analysis of the evolved DMS by purge-and-trap preconcentration has been used.

The P&T technique can also be applied for the determination of sulfur species in sediments.

Sulfur Compounds of Fossil Fuel-Origin

Trace level sulfur speciation and detection in crude oil and in different petroleum products is traditionally difficult due to the complex hydrocarbon matrix. Additionally, the fact that sulfur compounds are polar and the hydrocarbons matrices are non-polar favours the loss of sulfur compounds to active sites in analytical instruments and sample vessels. The development of sulfur-specific detectors for gas chromatography has added impetus to use of this technique for the analysis of petroleum fractions. For example, selectivity of the sulfur chemiluminescence detector (SCD) allows the determination of sub-ppm level of sulfur compounds in the presence of percent levels of co-eluting hydrocarbons.

The usual approach for characterization of the very complex nature of different individual sulfur compounds in a crude oil is to fractionate the oil into narrow boiling range cuts (prefractionation) and to analyse each fraction, which simplifies the analysis. Sample preparation/cleanup is needed, especially for analysis of high boiling fractions (coal-derived liquids, shale oil), before GC, Solid phase extraction (SPE), using various cartridges with different solvent mixtures, followed by normal-phase liquid chromatography has been applied for separation of polycyclic aromatic sulfur heterocyclic compounds (PASHs) from polycyclic aromatic hydrocarbons (PAHs). PASHs can be found not only in fossil fuels, but also in sediments, mussels, fish and airborne particulate matter. The separation and determination of individual alkyl-substituted PASHs isomers in environmental matrices is difficult because of the isomeric structures of these species due to asymmetry imposed by the sulfur atom. Relatively good resolution of many PASHs isomers has been obtained on a smectic liquid crystal column (**Figure 1**).

In research and in everyday practice, one frequently encounters situations where not only the concentrations of both sulfur and non-sulfur compounds but also both percentage levels and low concentrations (ppm and ppb levels) of sulfur species have to be determined. In such cases two parallel detectors can be used. For example, coupling of sulfur chemiluminescence (SCD) and thermal conductivity detectors (TCD) enables the determination of concentration of both sulfur-containing (from percentage to ppb levels) and other gaseous compounds through simultaneous sampling, separation, and detection. Also simultaneous SCD and FID detection can be useful in many cases.

The sulfur-selective detectors, mainly SCD and atomic emission detector (AED), can be interfaced to simulated distillation (SimDis) systems to measure the boiling point range distribution of heteroatoms (S and N) in various petroleum fractions. Such an approach is applied for process control, quality assurance and product specification purposes. Very good sulfur SimDis chromatograms have been obtained considering the fact that typical sulfur levels in refinery streams are several orders of magnitude lower than the hydrocarbon levels.

The sulfur-selective detectors have been used for oil spill identification by finger-printing of various crude oils. The specific identification of different dibenzothiophenes by GC–high resolution MS has

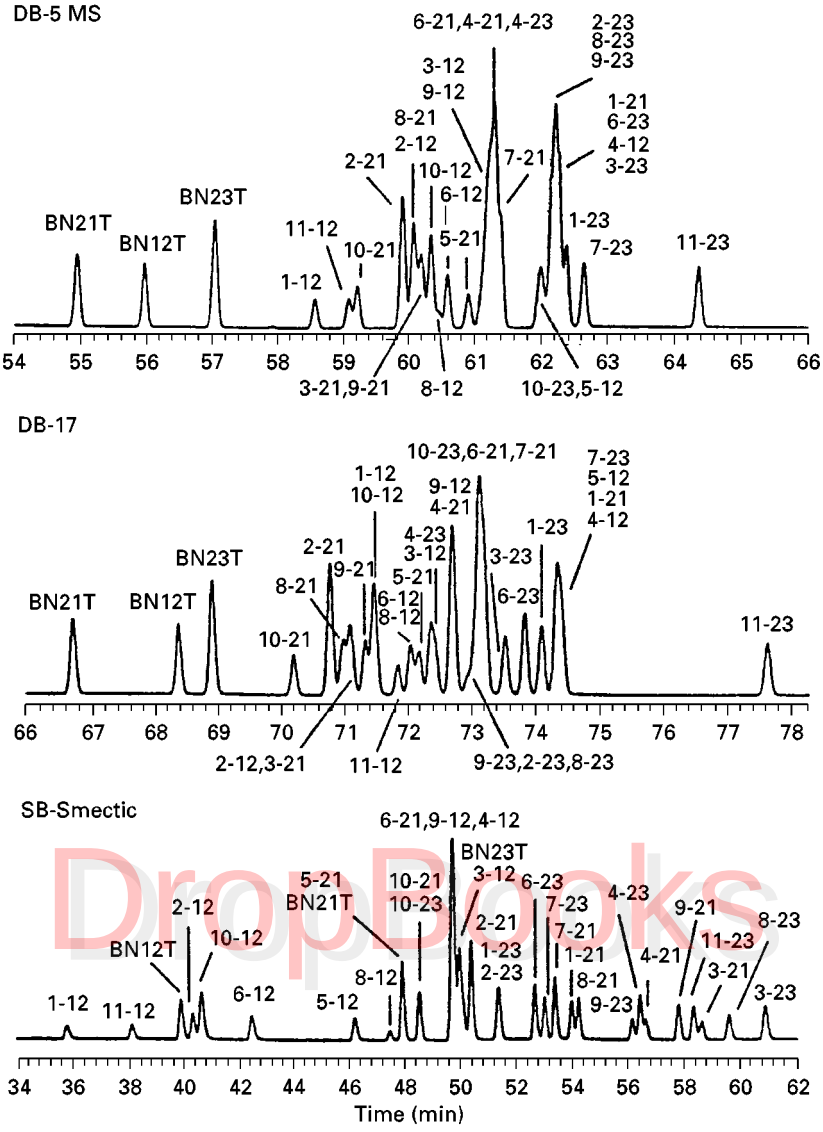

Figure 1 GC–MS separation of 3 benzo[*b*]naphthothiophene (BNT) (*m/z* 234) isomers and 30 methylbenzo[*b*]naphthothiophene (MeBNT) isomers (*m/z* 248) on different stationary phases: DB-5MS, DB-17 and SB-Smectic. BN12T = benzo[*b*]naphtho[1,2-*d*]thiophene, BN21T = benzo[*b*]naphtho[2,1-*d*]thiophene, and BN23T = benzo[*b*]naphtho[2,3-*d*]thiophene. Numbers identify the specific methylbenzo[*b*]naphthothiophene isomers, e.g., 1–12 = 1-methylbenzo[*b*]naphtho[1,2-*d*]thiophene, 8–21 = 8-methylbenzo[*b*]naphtho[2,1-*d*]thiophene, 11–23 = 11-methylbenzo[*b*]naphtho[2,3-*d*]thiophene, etc.

permitted differentiation of very similar crude oils, even from the same field.

The ability to speciate the sulfur compounds is an advantage of GC method over elemental analysis, but total sulfur can also be determined by GC by summation of all the sulfur-containing peaks.

Sulfur Compounds in Beverages and Foodstuffs

Volatile sulfur compounds have been detected in wine, beer (**Figure 2**), dairy products, coffee, fish, garlic and tobacco smoke. In food chemistry these compounds contribute significantly to odour and flavour because they often possess characteristic smells and sensory thresholds (ca. 1 $\mu g\,kg^{-1}$ for DMS).

For isolation of sulfur compounds from different food matrices, headspace sampling (HS) is the best method. For example, HS-GC has been used for the determination of VSCs in water–alcohol solutions nd brandies. It was found that headspace concentrations of sulfur, H_2S, MeSH, EtSH, DMS, CS_2, DES, thiophene, DMDS and DEDS increased with increasing ratio between the gas and liquid phase volumes and was proportional to the temperature. However, it

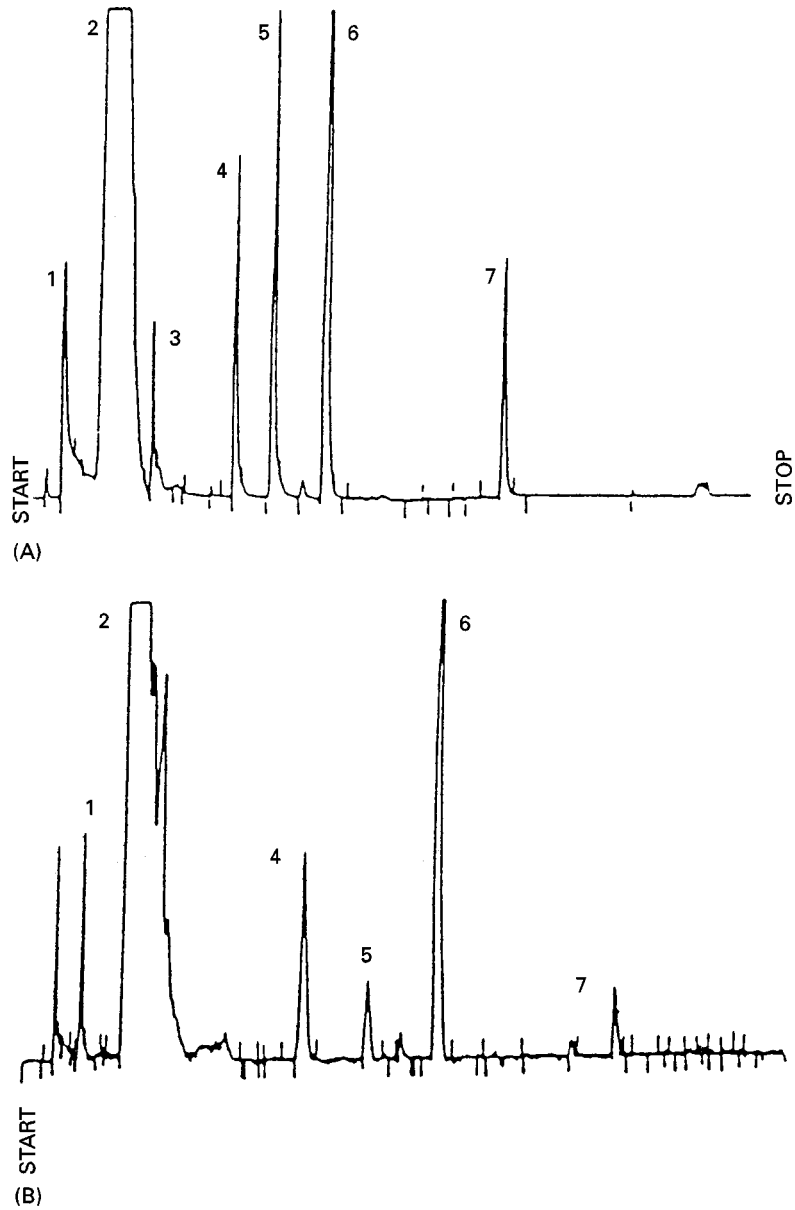

Figure 2 GC–SCD chromatograms of (A) a beer with a sulfury character and (B) a non-sulfury beer. GC conditions: column: DB-5, 30 m, 0.53 mm I.D., 1.5 μm film thickness: injector temperature: 150°C; column temperature programme: 20–50°C at 5°C min^{-1}, 50–180°C at 8°C min^{-1}, 10 : 1 split injection. Peaks: (1) methanethiol; (2) dimethyl sulfide; (3) ethylene sulfide; (4) diethyl disulfide; (5) dimethyl disulfide; (6) isopropyl sulfide (internal standard) and (7) dimethyl trisulfide.

diminished with increasing ethanol content and was insensitive to the liquid phase salt concentration. HS sampling has also provided qualitative and quantitative data of sulfur species in dairy products.

Storage Stability of Samples

In order to avoid losses or possible transformations of sulfur compounds, samples should be analysed as soon as possible. Keeping the samples at sub-ambient temperature can improve the stability of sulfur compounds. Sulfur concentrations in an air sample collected cryogenically and stored in a freezer were found not to change over a 2 week period. A Tenax trap containing VSCs collected from air was stored for at least 1 week at 196°C in liquid nitrogen without any loss of sulfur compounds.

For sulfur gases the most convenient method of storage seems to be in Tedlar bags. The concentrations of the five sulfur gases (COS, CS_2, MeSH and EtSH) in such bags were stable for two weeks even at the ppb concentration. Tedlar bags are not suitable for SO_2 and H_2S. In these cases, SO_2 concentration decreased from 22 ppb to less than 1 ppb in 2 h and

H_2S lost half of its original concentration of 70 ppb in about 10 days. The stability of sulfur gases in glass sampling bulbs is influenced by the gas matrix (nitrogen and air) and moisture. Reduced sulfur gases collected in glass bulbs can remain in the bulbs for approximately 24 h without major changes in gas concentrations if the sample is dry and does not contain oxygen (concentration decreased less than 5%) but dried air samples should be analysed within 3 h. Glass bulbs are not useful for collecting sulfur gases if the sample in the bulbs contains moisture (significant decrease in H_2S and MeSH concentrations was observed).

The stability of freshwater samples is strongly affected by the temperature at which it is stored. For example, it was reported that the stability of DMS in freshwater is shorter than the 48 h found in seawater samples.

Because the presence of reduced sulfur compounds in seawater is closely related to biological activity, the stability of samples may depend on the depth of sampling. When a sample was taken from the Baltic Sea at 4 m depth and was stored at 5°C in the dark, the concentration of DMS first rose dramatically after 4 days (nearly 10 times) and later decreased. Concentration of sample taken from 50 m depth did not change over a 2 week period. Samples can most probably be stored longer if the cold trap is maintained in liquid nitrogen.

To suppress microbial activity, compounds such as phenols, mercuric chloride, sodium azide and HCl can be added to water samples.

When immediate analysis is not possible, refrigeration of sample for analysis of sulfur compounds in aqueous solutions is recommended as the best way to maintain sample integrity at least for periods up to 48 h.

Separation Systems

Column packing for chromatographic determination should be chosen not only with respect to the complete separation of a given mixture but should also be selected with respect to minimize losses due to adsorption and catalytic reactions and rearrangements. These are particularly important when packed metal and glass column are used.

The most common material used for packed columns in the analysis of VSCs is Teflon. Supelpack S (specially treated Porapack QS), different Chromosorbs, Porapack Q, N or QS, Triton X 305, Chromosil 310 or 330 (specially treated silica gel), Carbopack B or BHT 100 and 3% polyphenyl ether and 1% phosphoric acid on Chromosorb T have all been reported for VSCs analysis.

Good separation of many gaseous sulfur compounds can be obtained on Chromosil 310 and 330 and Supelpack (Figure 3). The latter can resolve the

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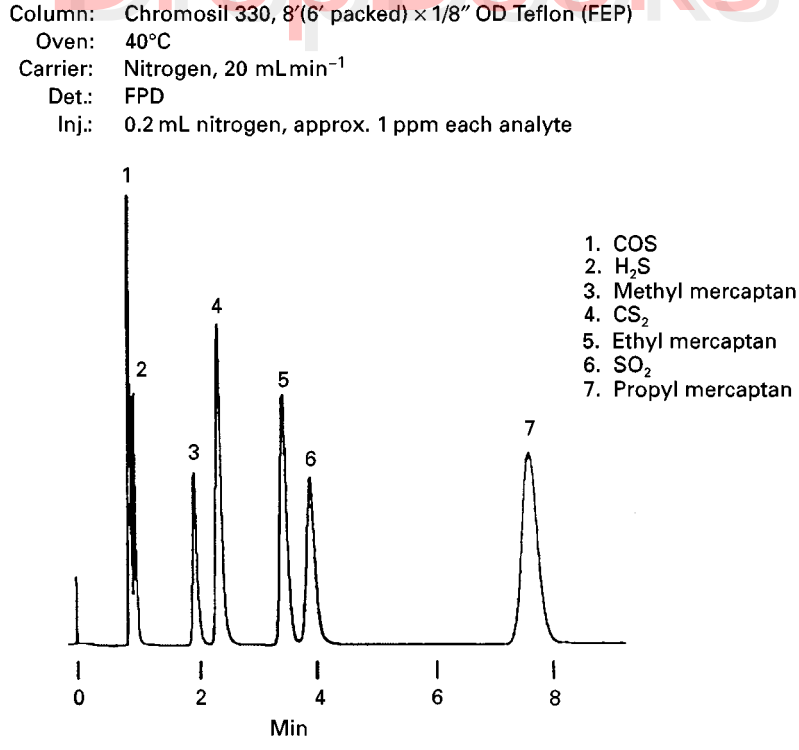

Figure 3 Trace light sulfur gases and C1–C3 mercaptans. (From Supelco Bulletin 722, reprinted with permission of Supelco, Bellefonte, PA 16823, USA.)

large peak of CO_2 (evolved from acidified seawater) from the much smaller and neighbouring H_2S and COS peaks.

Development of fused silica capillary columns has provided more inert surfaces for trace sulfur analysis. As with most analysis, no single capillary column can assure the combination of sample capacity, good resolution and reasonable analysis time for the wide range of sulfur species in different sample matrices. The analysis of VSCs has been achieved with methyl silicone phases like BD1 or Rtx1 with thick films (4–5 μm). Generally, columns with thicker films provide increased separation of volatile sulfur compounds and are better suited for analysis of low level volatile sulfur compounds in gases (**Figure 4**). On such non-polar columns retention times are governed primarily by boiling points and the retention sequence can be predicted from boiling-point data. Thick films separate most VSCs in programmed temperature analysis with an initial temperature of 40–50°C. For the separation of H_2S, COS and SO_2 sub-ambient column temperatures must be used (**Figure 5**).

Recently, porous layer open tubular (PLOT) columns have become commercially available. The usefulness of such columns has been demonstrated for analysis of sulfur compounds such as COS, H_2S and DMS.

Smectic liquid crystalline columns may offer unique selectivity for isomeric polyaromatic sulfur compound (PASHs) mixtures that are not possible with other columns. Unfortunately, extensive use of the SB-smectic column at the upper temperature limit (250°C isothermal, 270°C during temperature programmed) can reduce the useful lifetime and column selectivity often changes dramatically with use.

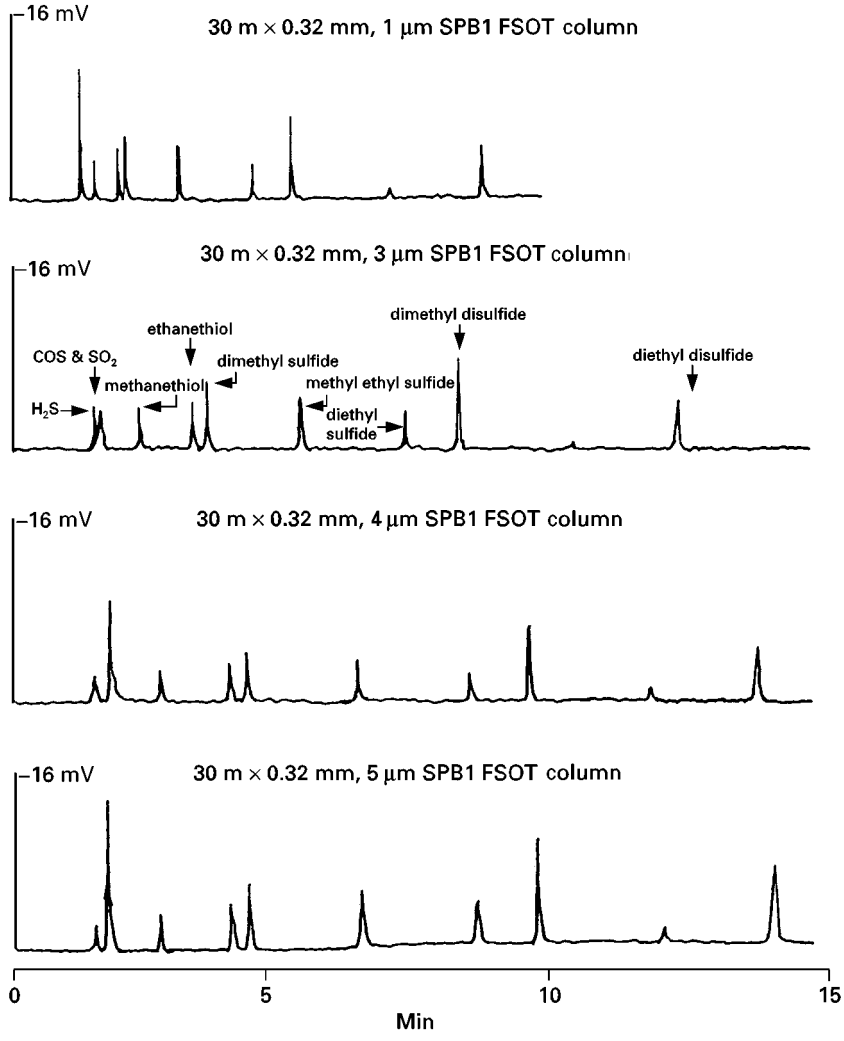

Figure 4 Effect of stationary film thickness on the separation of sulfur-containing compounds. Sample: gas phase standard of 10 component mixture of sulfur compounds: 1 mL split injection (split ratio 10 : 1), SCD, temperature programme 1 min at 35°C, 35–200°C at 10 min. Reproduced with permission from Hutte (1990).

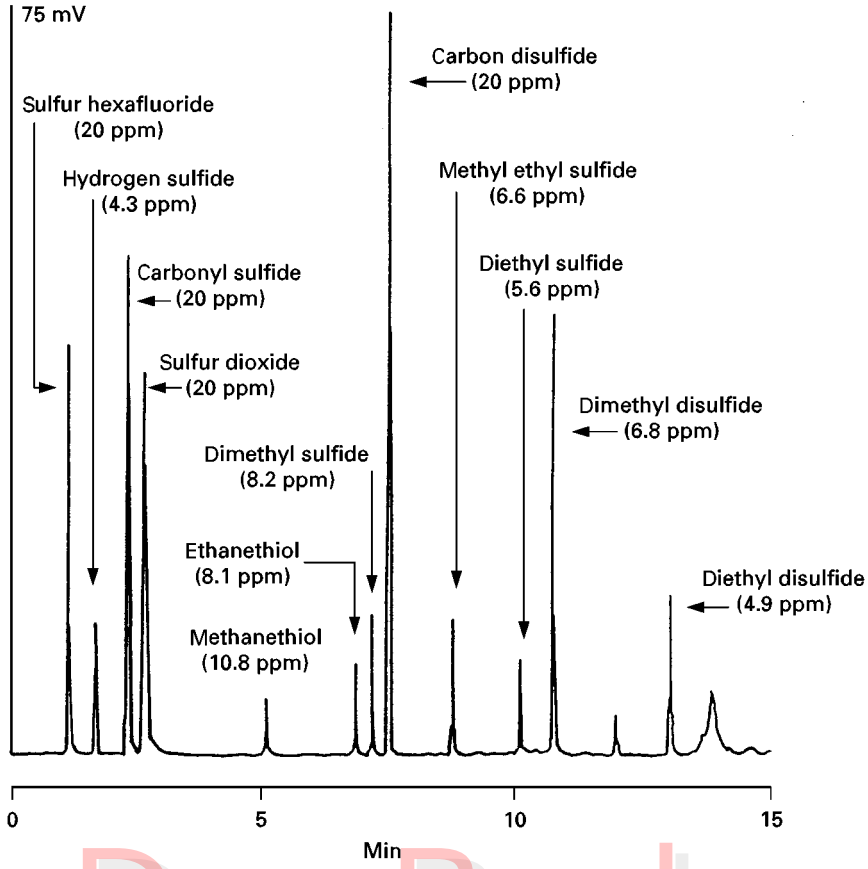

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Figure 5 Sub-ambient column temperature separation of sulfur gas standard: GC conditions: 1 mL split injection (split ratio 10 : 1), injection port at 250°C, FID temperature 300°C. Column temperature programme: 2 min at − 30°C, − 30–200°C at 20° min^{-1}. Detector conditions: SCD integration time 0.03 s. Reproduced with permission from Hutte (1990).

Detection Systems

The value of GC for sulfur compounds analysis is found in the availability of selective and sensitive detectors. These detectors are especially useful because matrices requiring sulfur analysis are often very complex. Such detectors can reduce the analysis time by eliminating laborious and time-consuming procedures of sample preparation, which can also often cause contamination or loss of analytes. Selective detectors have found extensive application in the determination of sulfur compounds in various matrices because of these reasons.

Table 1 lists the basic characteristics of the most frequently used sulfur-selective detectors.

The flame photometric detector (FPD) is still the most widely used sulfur selective detector. The FPD exhibits a non-linear (exponential) response to sulfur compounds and response factors may be compound-dependent but it is relatively inexpensive, robust and adequate for many applications. The major advantage of the FPD is its application to gases and fuels. However, major co-eluting hydrocarbons present in liquid fuels have a quenching effect on the sulfur response. Also the injection of aqueous samples directly into a GC-FPD system is not recommended because the injected water can extinguish the detector flame and non-volatile material contained in the sample can contaminate the injection port and column. An increase of the detector temperature prevents the flame from being extinguished but working at temperatures higher than 250°C may produce a poor baseline. An improved FPD called a pulsed flame photometer detector (PFPD) employs a pulsed flame and time-resolved emission detection with gated electronics. The improvements include one to two orders of magnitude sensitivity enhancement, about an order of magnitude of increased selectivity and reduced quenching effects.

A more recent alternative to the FPD is the sulfur chemiluminescence detector (SCD). Recent applications of this detector have shown that it gives good performance in terms of detectability, selectivity, linearity and a nearly equimolar response to sulfur. It does not suffer significantly from quenching or interferences. The combination of fused silica capillary

Table 1 Basic characteristics of gas chromatographic sulfur-sensitive detectors

Detector	*Detection limit [gS/s]*	*Selectivity [S/C]*	*Linear concentration range (decades)*	*Ease of operation*	*General characteristics*
FPD	10^{-11}	10^{-3}–10^{5}	3[a]	Moderate	Exponential and compound-dependent response, susceptible to flame-out and quenching effects
PFPD*	10^{-13}	10^{6}	3[a]	Moderate	Less quenching than for the regular FPD
ECD	Variable up to 10^{-15}	Variable	4	Simple	Strongly compounds-dependent response, very high sensitivity to SF_6 itself or post-column converted sulfur compounds
SCD** (flame version)	10^{-12}	$>10^{6}$	4–5	Moderate	Linear and nearly equimolar response, non-susceptible to quenching or interferences, very convenient for petroleum applications
SCD (non-flame version)	10^{-13}	$>10^{7}$	4–5	Simple	
AED***	10^{-12}	10^{4}	3–4	Difficult	Small susceptibility to quenching or interferences, possibility of elemental composition confirmation
HECD^{+}	10^{-11}	10^{4}–10^{6}	3–5	Complicated	Possible interferences of other organic compounds
PID^{++}	10^{-12}	Poor	6	Moderate	Many factors influence the detecter response
MS	10^{-11}	Specific	5	Complicated	Convenient for identification of complex mixture, new membrane techniques assure lower detection limit
FT-IR	10^{-12}	Specific	4	Complicated	Applied only for highly complex mixture. Strongly compound-dependent

[a]After linearization.
*Pulsed flame photometric detector.
**Sulfur chemiluminescence detector.
***Atomic emission detector.
$^{+}$Hall electrolytic conductivity detector.
$^{++}$Photoionization detector.

columns and the SCD provides a powerful tool for the measurements of trace levels of sulfur containing compounds in complex matrices (**Figure 6**). The performance of the SCD can be improved by changing the means of sulfur-chemiluminescent-species production from a hydrogen flame (commonly referred to as a flame SCD) to a closed hydrogen/air burner (a flameless SCD). The flameless SCD is typically an order of magnitude more sensitive than the flame version. An extremely low detection limit of 25 fgS/s has been reported but most authors have observed a limit between 0.1 and 1 pgS/s.

The atomic emission detector (AED) has a good combination of specificity and sensitivity for the analysis of volatile sulfur-containing compounds. The AED is better than the FPD because it does not exhibit as many problems with interferences, quenching, and compound-dependent responses. The AED can be used to confirm the elemental composition of a compound by its ability to monitor several atomic lines simultaneously. The response of the AED to sulfur at 180.7 nm is reported to have linear range of 2×10^4, and sensitivity of 1.7 pgS/s and a selectivity over carbon of 1.5×10^3.

The electrolytic conductivity detector (HECD or Hall detector) has found limited applications in analysis of VSCs probably because it requires regular attention. The electrolyte must be kept extremely clean and sulfur specificity is limited by high concentrations of co-trapped carbon dioxide. Despite these problems, the HECD performs well in the sulfur detection mode. The detector response is linear up to 50 ng sulfur, selectivity of sulfur to carbon is typically better than 10^4, and the limit of detection is 1 pgS/s.

The electron-capture detector (ECD) can also be used for determination of a variety of sulfur containing compounds, e.g., SO_2, H_2S, thiols and organic

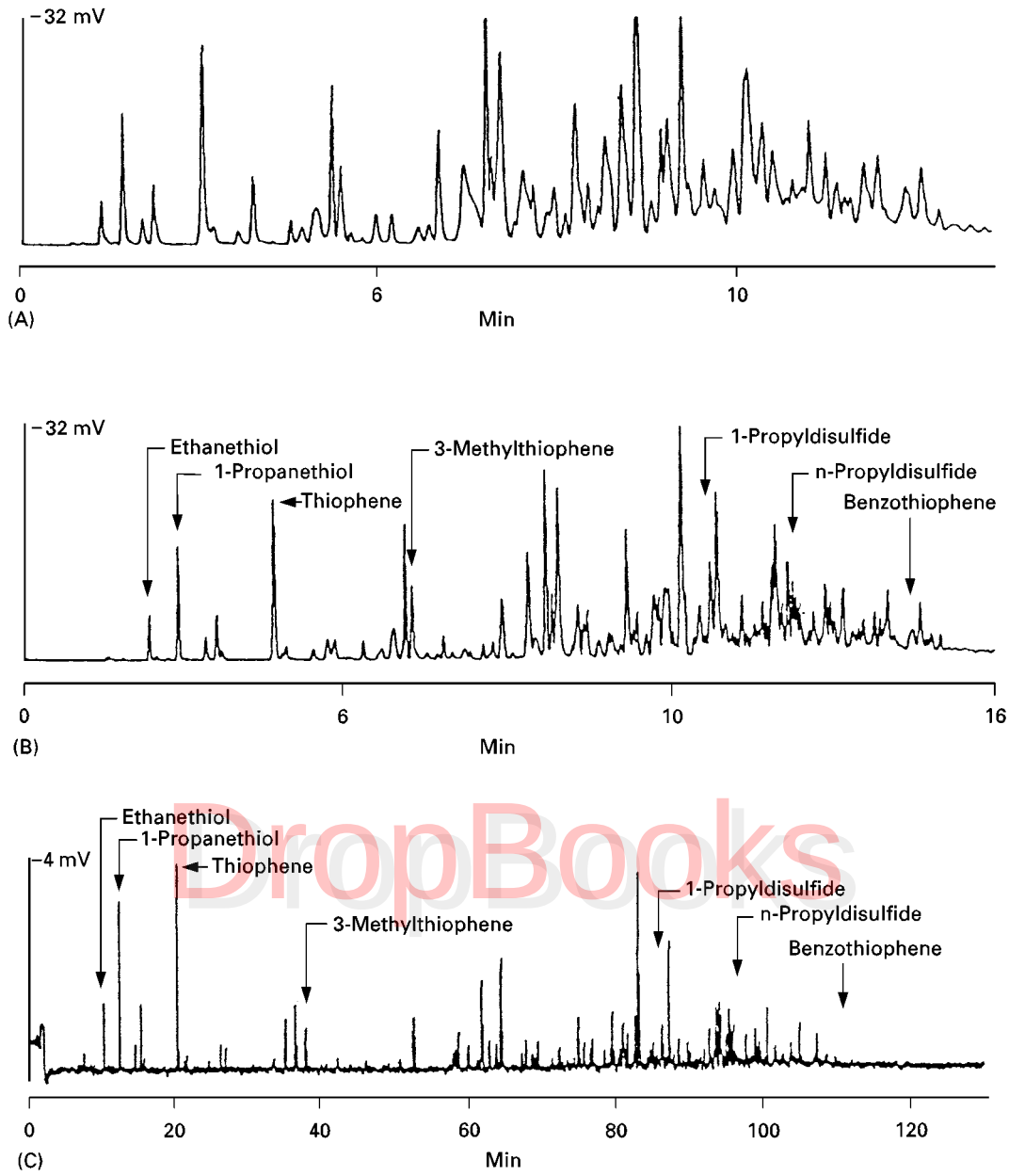

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Figure 6 Comparison of column resolution for the analysis of sulfur components of raw naphtha feedstock (SCD). Capillary columns: A: 15 m × 0.53 mm i.d. DB-1 (1.5 μm film thickness); B: 30 m × 0.32 mm i.d. SPB-1 (1 μm film thickness); C: 100 m × 0.25 mm i.d. SPB-1 (0.5 μm film thickness). GC conditions: 1 μL direct injection for column A, 1 μL split injection for column B (split ratio 10 : 1) and column C (split ratio 100 : 1). Injection port temperature 250°C. Column temperature programme: column A: 1 min at 35°C 35–200°C at 8° min^{-1}; column B: 1 min at 35°C, 35–200°C at 10° min^{-1}; column C: 13 min at 35°C, 35–45°C at 10°C min^{-1}, 15 min at 45°C, 45–60°C at 1°C min^{-1}, 60–300°C at 2°C min^{-1}. Reproduced with permission from Hutte (1990).

mono- and di- and trisulfides. Although the ECD is only moderately sensitive to SO_2 and H_2S, both are detected in the concentration range 0.1–1 μg g^{-1} in a 1 mL air sample. For COS, CS_2, MeSH, H_2S and DMDS the detector displays a sensitivity comparable to the FPD but is much less sensitive towards DMS and thiophene. SF_6 can be detected at extremely low levels with minimum detectable peaks lower than 0.2 fmol. The inertness and extremely low detectability of SF_6 has led to the development of a method in which the original sulfur compounds are fluorinated and then detected as SF_6.

The application of GC-MS systems is becoming more popular in the analysis of various sulfur compounds. Determination of sulfur compounds in underground reservoirs of natural gas and town gas (RSH, RSR and RSSR type compounds) by GC-MS has been carried out using the ion $CH_2 = S^+H$

Table 2 Representative examples of sulfur gas determination by gas chromatography

Matrix	*Analysed compounds*	*Sample preparation*	*Column*			*Temperature conditions*	*Detector*	*Detection limit*
			Material	*Packing*	*Dimension*			
Atmospheric sulfur gases	COS, MeSH, CS_2, DMS, SF_6	Chemisorption on gold wool + cryotrapping or only direct cryotrapping	Fused silica	BP-1	30 m × 0.32 mm × 1 μm	Isothermally, 35°C	AED	0.1 nmol m^{-3}
Air from a petroleum plant	H_2S, C_1–C_7 thiols, DMS	Trapping on Tenax TA, placed in PTV injector, cryotrapping on column	Fused silica	GS-Q	30 m × 0.53 mm	1 min at 100°C, 100–240°C at 8°C min^{-1}, 30 min at 240°C	FPD	pgS
Gases from sweetening process	H_2S, COS, CS_2, thiophene, MeSH, (ppm level) in CH_4, CO_2, C_2H_4 (% level)	Direct injection	Fused silica	CP-Sil 5CB	50 m × 0.32 mm × 0.5 μm	3 min at 75°C; 75–120°C at 20°C min^{-1}	SCD TCD	ppb level
			Stainless steel	Porapak Q	4 m × 3.2 mm o.d.	10 min at 120°C		
Gases from workplace environment	DMS, DES	Trapping on Tenax TA, cryofocusing (−150°C)	Fused silica	DB-1	15 m × 0.52 mm × 1.5 μm	2 min at 60°C; 60–100°C at 10°C min^{-1}, 1 min at 100°C; 100–250°C at 30°C min^{-1}	FPD + FID	μg m^{-3}
Atmospheric gas	DMS, DMDS in presence of volatile organic compounds	Cryogenic trapping on Tenax (Peltier effect)	Fused silica	Paraplot Q	10 m × 0.32 mm	7 min at 55°C; 55–216°C at 12°C min^{-1}	MS	ppt level
Tropospheric airborne gases	COS, H_2S, CS_2, DMS	Trapping in Teflon trap (liquid argon) After separation fluorination to SF_6					FPD MS ECD	ppt level
Atmospheric sulfur gases	H_2S, COS, SO_2, DMS MeSH, CS_2, DMDS EtSH, iPr SH	Cryogenic trapping in Teflon trap or in FSOT retention gap	Fused silica	DB-1/DB-Wax	30 m × 0.53 mm × 5 μm/ 3 m × 0.53 mm × 1 μm	1.2 min at 30°C; 30–140°C at 30°C min^{-1},	FPD	50 pgS
				DB-Wax	60 m × 0.53 mm × 1 μm	2 min at 30°C; 30–140°C at 15°C min^{-1}	MS	5 pgS
Antarctic atmosphere	SF_6	Sorption on Porapak Q (−77°C)	Stainless steel	Molecular sieve 5A	30 cm pre-column + 3 m	Isothermally, 65°C (back flushed when SF_6 reaches main column)	ECD	ppt level

Table 3 Representative examples of sulfur compound determinations in aqueous matrices by gas chromatography

Matrix	*Analysed compounds*	*Sample preparation*	*Column*			*Temperature conditions*	*Detector*	*Detection limit*
			Material	*Packing*	*Dimension*			
Antarctic marine waters	H_2S, COS, SO_2, MeSH, DMS	Purging, preconcentration on Tenax TA (ambient temperature), thermal desorption	Teflon	Carbopack B/1.5% XE 60/1% H_3PO_4	3 m × 0.25 mm	40–140°C–temperature programming	FPD	6–160 ng L^{-1}
Atlantic surface water	DMS, DMDS, CS_2, dimethyl selenide, dimethyl iodide	Purging, trapping in cold trap	Fused silica	SE-54	50 m × 0.32 mm × 5 μm	3 min at 70°C, 70–180°C at 3°C min^{-1}	AED or ECD	0.5–0.8 ppm
Aqueous matrices (distilled water, tap water, kraft mill condensate)	H_2S, MeSH, DMS, DMDS	Filtration with glass fibre filters, direct injection split mode (10 : 1)	Fused silica	DB Wax	30 m × 0.53 mm × 1 μm	5 min at 40°C; 40–160°C at 30°C min^{-1}, 3 min at 160°C, 160–200°C at 40°C min^{-1}	FPD	0.3 mg L^{-1}
Heavily polluted water	H_2S, COS, MeSH, DMS, CS_2, DMDS	Purging, cryogenic trapping (−80°C)	Teflon	Carbopack BHT-100	1.4 m × 3 cm	1 min at 5°C; 5–50°C at 30°C min^{-1}, 2 min at 50°C; 50–100°C at 30°C min^{-1}; 7 min at 100°C	FPD	ng S
Water samples, sediments	H_2S, COS, MeSH, DMS, CS_2, DMDS	Purging, cryocondensation secondary cryofocusing	Teflon	Carbopack BHT-100	1.4 m × 3.2 cm	−5–100°C at 30°C min^{-1}, 8 min at 100°C	FPD	pg S
Surface and potable water, industrial effluents, sediments	21 organosulfur compounds (thiophenes, sulfides, sulfones, benzothiazole)	Purging, trapping on Tenax, extraction with hexane or methylene chloride	Fused silica	DB-5	25 m × 0.25 mm × 0.33 μm	4 min at −50°C, −50–200°C at 16°C min^{-1}, 8 min at 200°C; 200–220°C at 16°C min^{-1}	MS	ppb level
Anoxic-lake water	H_2S, COS, MeSH, CS_2, EtSH, DMS	Purging, cryotrapping on Tenax TA (solid CO_2), heating with hot air (200°C)	Glass	UCON 50 HB 5100	25 m and 50 m	0°C–45°C at 3°C min^{-1}	FPD, MS	ng L^{-1}

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Table 4 Representative examples of sulfur compounds determination in beverages and food stuff by a gas chromatrography

Matrix	*Analysed compounds*	*Sample preparation*	*Column*			*Temperature conditions*	*Detector*	*Detection limit*
			Material	*Packing*	*Dimension*			
Garlic samples (whole non-peeled, peeled cloves, crushed cloves, juices)	15 sulfides, disulfides and trisulfides	Head space (5 and 45 min)	Fused silica	HP-5	25 m × 0.31 mm × 0.53 μm	2 min at 40°C, 40–70°C at 3°C min^{-1}, 70–205°C at 7.5°C min^{-1}; 205–250°C at 25°C min^{-1}	AED and MS	
Beer, coffee	13 volatile sulfur compounds, DMS DMDS, CS_2, other sulfides, C_1–C_4 thiols	200 μL of beer + 10 mL of water–silicone mixture, purging (85°C), cryogenic trapping (−170°C) 0.5 g coffee powder + 10 mL hot water, purging (85°C), (−170°C)	Fused silica	HP-1	25 m × 0.32 mm × 0.17 μm	1 min at −20°C, −20 to −10°C at 10°C min^{-1}, −10 to −40°C at 30°C min^{-1}, 40–150°C at 70°C min^{-1}	MIP-AED	from 0.4 ng L^{-1} for EtSH to 0.9 ng L^{-1} for DMS
Grape juice	COS, CS_2, DMS	Head space	Glass	Porapak QS		5 min at 80°C; 80–120°C at 12°C min^{-1}	FPD	
Alcoholic beverages	H_2S, MeSH, EtSH, DMS, CS_2, ethyl-methyl sulfide, DES, DMDS, DEDS	Head space	Fused siliica	SPB-1-Sulfur	30 m × 0.32 mm × 4 μm	1 min at 35°C; 35–55°C at 10°C min^{-1}, 55–250°C at 25°C min^{-1}	SCD	10 μg L^{-1}
Packaged food (wine, orange juice)	SO_2 in presence of CO_2 and H_2O	Head space	Teflon	Chromosorb 108	1.2 m × 2 mm	90°C and 120°C	HECD	0.81 ng L^{-1}

Table 5 Representative examples of sulfur compounds determination in fossil fuel related samples by gas chromatrography

Matrix	*Analysed compounds*	*Sample preparation*	*Column*			*Temperature conditions*	*Detector*	*Detection limit*
			Material	*Packing*	*Dimension*			
Gases from plasma reactors (also atmosphere from microelectronic processes and polluted air)	H_2S, COS, SO_2, CS_2, thiols, sulfides in the presence of C_1–C_5 hydrocarbons (HC)	Vacuum extraction from reaction tube or direct injection from pressurized cylinders and syringes	Teflon	Chromosorb 105	80 cm × 2 mm	1 min at 60°C, 60–180°C at 20°C min^{-1}, 2 min at 180°C	FID and FPD	10^{-10} gS/s 10^{-12} gHC/s
Natural gas	H_2S, SO_2, CS_2, C_1–C_4 thiols, DMS, DMDS, DEDS, methylethylsulfide, 2-ethylthiophene	Direct injection, split mode, 10 : 1	Fused silica	SPB-1 Sulfur	30 m × 0.32 mm × 4 μm	3 min at 10°C, 10–300°C at 10°C min^{-1}	SCD and FID	
Light petroleum fractions (cracked gasolines, diesels)	Thiophene, benzothiophene, dibenzothiophene and their alkyl substituted homologues	Direct injection, split mode, 10 : 1	Fused silica	DB-1	60 m × 0.25 mm × 0.25 μm	35–100°C at 10°C min^{-1}, 100–225°C at 2°C min^{-1}, 20 min at 225°C	SCD and FID	0.01% (w/w) of total S
Hydrotreated naphtha	H_2S, thiophene, alkylthiophenes, thiols	Direct injection, split mode, 1 : 100	Fused silica	SPB-1	30 m × 0.32 mm × 4 μm	35–125°C at 30°C min^{-1}, 125–260°C at 5°C min^{-1}	AED	H_2S-single ppm thiols-tens ppm total S-hundreds ppm
Commercial diesel fuels	Thiophene, benzothiophene, dibenzothiophene, hiolur sulfides (up to C_{16}) higher thiols (up to C_8)	Direct injection after dilution with n-hexane (1 : 100), on-column mode	Fused silica	HP-5	25 m × 0.32 mm × 0.52 μm	50–110°C at 30°C min^{-1}, 110–210°C at 2.5°C min^{-1}, 210–280°C at 2°C min^{-1}, 5 min at 280°C	FPD	
Fossil fuels (coal tar, crude oil)	80 polycyclic aromatic sulfur heterocyclic compounds (3–5 rings)	Prefractionation solid-phase extraction, LC clean-up	Fused silica	DB-5MS	60 m × 0.25 mm × 0.25 μm	1 min at 60°C, 60–150°C at 45°C min^{-1}, 2 min at 150°C; 150–300°C at 2°C min^{-1}, 25 min at 300°C	MS	Only for retention indexes determination
				DB-17		1 min at 60°C, 60–90°C at 35°C min^{-1}, 1 min at 190°C, 190–320°C at 1°C min^{-1}		
				Liquid crystalline polysiloxane (SB-Smectic)		1 min at 60°C, 60–190°C at 35°C min^{-1}, 1 min at 190°C, 190–266°C at 1°C min^{-1}		

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with m/z 47. The ion with m/z 45 is more intense in some sulfur compounds, but is often found in oxygen compounds ($C_2^+H_4OH$) as well. Twenty-one organosulfur compounds (DMS and DMDS among others) were detected in the approximate concentration range 0.1 to 2000 ppb in water, industrial effluent, sediment and fish samples using an automated GC-MS system. A GC-MS method for DMS and SO_2 determination in air in real time at the sub parts per trillion level with a high pressure selected-ion chemical ionization flow reactor has been developed. The use of isotope dilution GC-MS with perdeutered DMS for DMS determination in sea water gives better than 2% precision. By using the ratio of the MS response at m/z 62 and m/z 68, compensation can be made for instrumental drift as well any losses in sampling ambient air. Another significant advantage is the ability to determine DMS concentration by stripping only a small fraction of DMS from solution, resulting in artefact-free DMS concentration. In addition, larger volumes of water can be sampled by eliminating the need for long sampling periods required to remove DMS quantitatively from solution. Highly sensitive and specific continuous measurement of DMS in air, using triple quadrupole mass spectrometry with atmospheric pressure chemical ionization, has been demonstrated. Detection limits in continuous direct monitoring were determined for DMS (24 pptv), H_2S (1 ppbv), for MeSH, COS and CS_2 (about 10 ppbv).

Calibration

The preparation of reliable standard mixtures is an important step in analysis. The simplest way to calibrate a GC system for gas analysis is by injecting a suitable volume of a standard gas. Low concentration standards, usually needed in trace analysis, can be obtained by applying the exponential dilution flask technique or with permeation tubes. To minimize non-linear response problems (as for flame photometric detector) the calibration curves should cover the anticipated concentration range. For calibration, the gases from diffusion tubes are diluted with an inert gas and frequently led through a glass loop injected onto the column with appropriate valves. A new concept for the generation of standard mixture of thiols, based on thermal decomposition of a substance chemically bonded to the surface of silica gel, has been developed. The method enables preparation of a standard mixture containing volatile, malodorous, unstable and toxic compounds. For example, standard mixture of MeSH and PrSH have been generated by heating silica gel with anchored dithiocarbamate groups.

In analysis of liquids, primary standards are usually prepared in an appropriate solvent which should not interfere with the determined compounds. All standard solutions should be stored in vials with headspace volume as small as possible and kept at low temperature ($\leq 4^{\circ}C$).

Examples of Applications

Due to the diversity of sulfur compounds and various matrices in which they can be present, the chromatographer is faced with a difficult task when separation, identification and quantification of specific sulfur species are desired. The approach needed for the analysis of these compounds depends on several factors. In choosing the appropriate procedure, the analyst should consider the form of sulfur compounds to be determined, their levels of concentrations, the physical state and the complexity of the matrix. **Tables 2–5** present representative examples of sulfur compounds determination in various matrices using gas chromatography. The examples include sample preparation techniques, columns with chromatographic conditions, and detectors.

Conclusions

Gas chromatography, especially high resolution gas chromatography, perhaps more than other methods, fulfils the requirements needed for the analysis and structure elucidation of multicomponent environmental mixtures in which different sulfur species can be present in nanogram or picogram amounts. It should be noted that, besides selective high resolution columns and sensitive sulfur-specific detectors, most qualitative and quantitative determination of sulfur-containing compounds requires efficient sample enrichment techniques and quantitative desorption from traps. The applied procedure should also minimize adsorption losses of the sulfur compounds in the whole analytical system and reduce possible rearrangements of sulfur analytes. Significant progress is still being made in all steps of sulfur analysis in various environmental matrices but such procedures are not still routinely applied in many laboratories. Future developments should be focused on procedures that can be used during long research expeditions, directly aboard ships, or in situ for real-time measurements.

See Colour Plate 119.

See also: **II/Chromatography: Gas:** Detectors: General (Flame Ionization Detectors and Thermal Conductivity Detectors); Detectors: Mass Spectrometry; Detectors: Selective; Gas-Solid Gas Chromatography; Headspace Gas Chromatography; Multidimensional Gas Chromatography;

Sampling Systems. **III/Flavours: Gas Chromatography. Appendix 2: Essential Guides to Method Development in Gas Chromatography.**

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SUPERCRITICAL FLUID CRYSTALLIZATION

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Introduction

Supercritical crystallization processes use the special properties of supercritical fluids that make these fluids particularly suitable as solvents or antisolvents. In both cases, an expansion of a solution is used to create supersaturation, which is the driving force for nucleation and growth of the solute.

A supercritical fluid (SCF) is a fluid above its critical temperature and pressure. It is characterized by physical properties (such as viscosity and diffusivity) that can be continuously varied between those of liquids and gases. The liquid-like density of a SCF is associated with its ability to dissolve solutes, and hence its solvent power. Since this density can be changed significantly by changing the pressure and temperature in the critical region, the solvent properties of a supercritical fluid can be tailored for specific applications. **Figure 1** shows the relationship between pressure and density of carbon dioxide. The region above the critical pressure and temperature (7.38 MPa, 302.3 K) is commonly referred to as the supercritical region of carbon dioxide. It is important to note that the largest changes in the fluid density with changes in temperature and/or pressure in the single-phase region occur near the critical point. Therefore, large changes of solvent power can be achieved with small changes in pressure or temperature in the critical region. It should be added here that a supercritical crystallization process involves mixtures of solute and solvent; however, these mixtures are generally dilute so that their critical points are close to the critical point of the solvent. The behaviour depicted in Figure 1 may therefore be considered to be representative of the behaviour of dilute mixtures of constant composition.

If a supercritical fluid loaded with solute is expanded, then the resulting change in density may lead to precipitation of the solute. If these changes in density are made to occur rapidly, then the process is known as the rapid expansion of supercritical solutions, or RESS. Very high supersaturations may be achieved in RESS processes over a very short period of time. This generally favours the deposition of small crystals and narrow size distributions. Also, the crys-